

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-083818

(43)Date of publication of application : 31.03.1998

---

(51)Int.Cl.

H01M 4/62  
H01M 4/02  
H01M 4/58  
H01M 10/40

---

(21)Application number : 08-236160

(71)Applicant : HITACHI LTD

(22)Date of filing : 06.09.1996

(72)Inventor : YOSHIKAWA MASANORI  
IGAWA MICHIO  
YAMAUCHI SHIYUUKO  
ANDO HISASHI  
MURANAKA TADASHI  
DOSONO TOSHINORI

---

(54) LITHIUM SECONDARY BATTERY

(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a lithium secondary battery having excellent fast discharge characteristic and also high capacity by using a composite material of a graphite-type carbon material or an amorphous-type carbon material as a conductive agent for a cathode active material.

**SOLUTION:** As a material to be compounded with graphite or amorphous carbon, a mix produced by adding a binder and a cathode active material to metals, oxides, nitrides, carbides, borides, or silicides is applied and pressed. Consequently, a cathode in which electron conductivity with little anisotropy and high electron conductivity in the thickness direction in the electrode can be obtained. As a result, a battery having stable characteristic against the consumption at high current at the time of starting of a portable appliance or at the time of starting of an electric automobile can be obtained.

## \* NOTICES \*

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

## CLAIMS

---

### [Claim(s)]

[Claim 1] In a lithium secondary battery which comprises a negative electrode, an anode, and nonaqueous electrolyte containing lithium salt, A lithium secondary battery using a composite material with at least one sort of compounds, a black lead system carbon material, or a noncrystal carbon material selected from a metallic oxide, a nitride, carbide, a boride, or a silicide for a conducting agent of positive active material in the above-mentioned anode.

[Claim 2] In claim 1, The above-mentioned positive active material  $\text{LiNiO}_2$ ,  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNi}_{1-x}\text{Me}_x\text{O}_2$ ,  $\text{LiCo}_{1-x}\text{Me}_x\text{O}_2$ , or  $\text{LiMn}_{2-x}\text{Me}_x\text{O}_4$  (a transition metal Me:.) Or a lithium secondary battery which comprises at least one sort of compounds selected from 3B elements.

[Claim 3] A lithium secondary battery which comprises at least one sort of metal in which the above-mentioned metal was chosen from Ta, Ti, Zr, or aluminum in claim 1.

[Claim 4] In claim 1, The above-mentioned oxide  $\text{CrO}_2$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{IrO}_2$ ,  $\text{MoO}_2$ ,  $\text{NbO}$ ,  $\text{NbO}_2$ ,  $\text{OsO}_2$ ,  $\text{PtO}_2$ ,  $\text{ReO}_2$ ,  $\text{ReO}_3$ ,  $\text{RhO}_2$ ,  $\text{RuO}_2$ ,  $\text{Ti}_4\text{O}_7$ ,  $\text{WO}_2$ ,  $\text{W}_{18}\text{O}_{49}$ ,  $\text{V}_2\text{O}_3$ ,  $\text{V}_4\text{O}_7$ ,  $\text{V}_5\text{O}_9$ ,  $\text{V}_6\text{O}_{11}$ ,  $\text{V}_7\text{O}_{13}$ , A lithium secondary battery which comprises at least one sort of oxides selected from  $\text{V}_8\text{O}_{15}$  or  $\text{V}_6\text{O}_{13}$ .

[Claim 5] A lithium secondary battery which comprises at least one sort of nitrides in which the above-mentioned nitride was chosen from BN, NbN,  $\text{Ta}_2\text{N}$ , TiN, VN, or ZrN in claim 1.

[Claim 6] A lithium secondary battery which comprises at least one sort of carbide in which the above-mentioned carbide was chosen from  $\text{B}_4\text{C}$ , HfC, MoC, NbC, SiC, TaC, TiC, VC, WC, or ZrC in claim 1.

[Claim 7] A lithium secondary battery which comprises at least one sort of borides in which the above-mentioned boride was chosen from  $\text{CrB}_2$ ,  $\text{HfB}_2$ , MoB, NbB, TaB,  $\text{TiB}_2$ , or  $\text{ZrB}_2$  in claim 1.

[Claim 8] A lithium secondary battery which comprises at least one sort of silicides in which the above-mentioned silicide was chosen from  $\text{MoSi}_2$ ,  $\text{NbSi}_2$ ,  $\text{TaSi}_2$ ,  $\text{TiSi}_2$ ,  $\text{VSi}_2$ , or  $\text{WSi}_2$  in claim 1.

[Claim 9] A lithium secondary battery with which the above-mentioned negative electrode comprises at least one sort of materials selected mainly from amorphous substance system carbon, black lead system carbon, metal support amorphous substance system carbon, or metal support black lead system carbon in claim 1.

[Claim 10] A portable information-and-telecommunications terminal equipment, portable video, and a personal computer using the above-mentioned cell according to claim 1 as a power supply.

[Claim 11] Consumer electronics using the above-mentioned cell according to claim 1 as a power supply.

[Claim 12]An electric power storage system for electric power using the above-mentioned cell according to claim 1 as a power supply.

[Claim 13]An electromobile using the cell according to claim 1 as a power supply.

---

[Translation done.]

## \* NOTICES \*

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

## DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the lithium secondary battery which used nonaqueous electrolyte.

[0002]

[Description of the Prior Art] Although it is expected that the spread of a personal computer, cellular phones, etc. will increase increasingly with development of an information society from now on, in connection with this, high-energy-density-izing of the cell which is a power supply of a portable equipment, and high capacity-ization are demanded increasingly. Since cell voltage is high energy density highly, development is prosperous in the lithium secondary battery using nonaqueous electrolyte, and it also has some cells put in practical use.

[0003]

[Problem(s) to be Solved by the Invention] As for the conventional cell, carbon black (JP,6-26124,B) of black lead (JP,5-52026,B) or an amorphous carbon system is used for the conducting agent of the electrode. However, a cell with high power density is required to carry a cell as a power supply of a personal computer, a cellular phone, portable video equipment, etc. That is, since a high current is consumed at the time of starting of these apparatus, the battery capacity which is equal to quick discharge is required. Also in a large-sized cell, the output very big, for example at the time of start in an electromobile is required, and good quick discharge performance is required. When black lead or amorphous carbon is used, sufficient discharge characteristic is not obtained. For example, if a discharge rate is raised to 2C (30 molar fractions) from 0.25C (four hour rates), service capacity will fall about 20 to 30%. Thus, if a discharge rate is raised, the battery life with which a cycle characteristic also falls to and it can be satisfied of a cycle characteristic in connection with it will no longer be acquired. It is thought that the factor which influences such a discharge characteristic has the most dominant electron conductivity in the electrode of an anode. Although what is necessary is just to make the quantity of black lead or amorphous carbon which is a conducting agent increase to aiming at improvement in the electron conductivity in an electrode, since the rate of the conducting agent occupied to an electrode in that case becomes large, the volume energy density which is one of the important characteristics of a cell falls. That is, maintaining high volume energy density, when raising the electron conductivity in an electrode develops a practical cell, it is important.

[0004] The purpose of this invention has good quick discharge characteristics, and there are in providing the

lithium secondary battery which is moreover high capacity.

[0005]

[Means for Solving the Problem] In order to solve a technical problem mentioned above, development of conducting agents other than black lead from the former or amorphous carbon is indispensable. Crystal structure of black lead is stratified and it is two-dimensional in an electronic conduction mechanism reflecting the structure. That is, although electron conductivity within a side is good, face-to-face electrical conductivity is very low, and is large. [ of the anisotropy of electronic conduction ] Since graphite powder is a scale-like when a mixture which consists of black lead, positive active material, and a binder is applied and pressed in aluminium foil or stainless steel foil of a charge collector, it is easy to carry out orientation of the high a side of electron conductivity to parallel with foil, and there is a tendency for the electron conductivity of a thickness direction in an electrode to fall easily. For this reason, when charge and discharge are performed at a high rate, sufficient charging and discharging characteristic is not acquired. On the other hand, amorphous carbon has the point that specific surface area was very greatly excellent considering a touch area with an active material as a conducting agent made greatly, and the anisotropy of electron conductivity also has a small advantage as compared with black lead. However, there is a fault whose electron conductivity is lower than black lead.

[0006] In order to improve a fault of such black lead or amorphous carbon, as a result of examining many things, it has electron conductivity and improvement in a remarkable discharge characteristic was accepted by moreover using a composite material with material with the small anisotropy of the electron conductivity, black lead, or amorphous carbon for a conducting material. Materials, such as metal, an oxide, a nitride, carbide, a boride, or a silicide, are preferred for black lead or amorphous carbon, and composite-ized material. Unlike a case where black lead is used, the anisotropy of electron conductivity in an electrode can obtain a high anode of the electron conductivity of a thickness direction in an electrode small by applying and pressing a mixture which added a binder and positive active material in such composite-ized materials. When it is made to composite-ize using material whose electron conductivity is higher than amorphous carbon, electron conductivity in an electrode can be improved employing the feature of amorphous carbon with large specific surface area efficiently.

[0007] Metal used for composite-ization of this invention Ta, Ti, Zr, or aluminum, An oxide  $\text{CrO}_2$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{IrO}_2$ ,  $\text{MoO}_2$ ,  $\text{NbO}$ ,  $\text{NbO}_2$ ,  $\text{OsO}_2$ ,  $\text{PtO}_2$ ,  $\text{ReO}_2$ ,  $\text{ReO}_3$ ,  $\text{RhO}_2$ ,  $\text{RuO}_2$ ,  $\text{Ti}_4\text{O}_7$ ,  $\text{WO}_2$ ,  $\text{W}_{18}\text{O}_{49}$ ,  $\text{V}_2\text{O}_3$ ,  $\text{V}_4\text{O}_7$ ,  $\text{V}_5\text{O}_9$ ,  $\text{V}_6\text{O}_{11}$ ,  $\text{V}_7\text{O}_{13}$ ,  $\text{V}_8\text{O}_{15}$  or  $\text{V}_6\text{O}_{13}$ , A nitride BN, NbN,  $\text{Ta}_2\text{N}$ , TiN, VN, or ZrN, Carbide  $\text{B}_4\text{C}$ , HfC, MoC, NbC, SiC, TaC, TiC, VC, WC, or ZrC, A boride  $\text{CrB}_2$ ,  $\text{HfB}_2$ , MoB, NbB, TaB,  $\text{TiB}_2$ , or  $\text{ZrB}_2$ ,  $\text{MoSi}_2$ ,  $\text{NbSi}_2$ ,  $\text{TaSi}_2$ ,  $\text{TiSi}_2$ ,  $\text{VSi}_2$ , or  $\text{WSi}_2$  is preferred for a silicide. An anode can be constituted by using these compounds, a black lead system carbon material or an amorphous substance system carbon material, and composite-ized material for a conducting agent, and applying and pressing positive electrode mixture which added and kneaded a binder and positive active material to this in aluminium foil or stainless steel foil. Positive active material  $\text{LiNiO}_2$ ,  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNi}_{1-x}\text{Me}_x\text{O}_2$ ,  $\text{LiCo}_{1-x}\text{Me}_x\text{O}_2$ , or  $\text{LiMn}_{2-x}\text{Me}_x\text{O}_4$  (a transition metal Me:.) Or a compound chosen from lithium containing transition metal oxides, such as at least one etc. sort, at least one or more sorts can be used out of 3B element.

[0008] On the other hand, even if an amorphous substance system carbon material, a black lead system

carbon material, a metal support amorphous substance system carbon material, or a metal support black lead system carbon material is preferred for a negative electrode and it uses any of such materials, the purpose of this invention is attained.

[0009]An electrolyte, For example, propylene carbonate, a propylene carbonate derivative, ethylene carbonate, butylene carbonate, vinylene carbonate, dimethyl carbonate, diethyl carbonate, methylethyl carbonate, 2-methyltetrahydrofuran, dioxolane, A tetrahydrofuran, a tetrahydrofuran derivative, 1, 2-dimethoxyethane, 1,2-diethoxyethane, 1,3-dioxolane, a formamide, dimethylformamide, gamma-butyrolactone, dimethylsulfoxide, acetonitrile, nitromethane, methyl formate, methyl acetate, methyl propionate, ethyl propionate, trialkyl phosphate, trimethoxy ethane, To a nonaqueous solvent chosen from a dioxolane derivative, diethylether, 1,3-propane Salton, sulfolane, 3-methyl-2-oxazolidinone, these halogenides, etc. at least one sort. For example,  $\text{LiClO}_4$ ,  $\text{LiAlCl}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiSbF}_6$ ,  $\text{LiB}_{10}\text{C}_{10}$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiCF}_3\text{CO}_2$ , A solid electrolyte which has the conductivity of organic electrolysis liquid in which lithium salt chosen from  $\text{LiCl}$ ,  $\text{LiBr}$ ,  $\text{LiI}$ , low-grade aliphatic-carboxylic-acid lithium, chloroboranelithium, 4 phenyl lithium borate, etc. at least one sort was dissolved, or a lithium ion. Or a known electrolyte used by cells generally using a carbon system material, a lithium metal, or a lithium alloy as negative electrode active material, such as a gel electrolyte or fused salt, can be used. Even if it uses a microporous separator according to the constitutional necessity for a cell, an effect of this invention is not spoiled at all.

[0010]Although a use in particular of a cell of this invention is not limited, For example, a notebook computer, a pen input personal computer, a pocket personal computer, a note type word processor, a pocket word processor, an Electronic Book player, a cellular phone, a cordless phone cordless handset, a pager, a handy terminal, a portable copy, an electronic notebook, a calculator, a liquid crystal television, an electric shaver, a power tool, A power supply for apparatus, such as an electronic translating machine, a car telephone, a transceiver, a voice input machine, a memory card, a backup power supply, a tape recorder, radio, a headphone stereo cassette tape recorder, a portable printer, a handy cleaner, portable CD, a video movie, and a navigation system, It can be used as a power supply of a refrigerator, an air-conditioner, television, a stereo, a calorifier, an oven microwave oven, a dishwasher, a washing machine, an oven, a game machine machine, lighting apparatus, a toy, a load conditioner, medical equipment, an electromobile, a golf cart, an electric cart, etc. It is usable to a system for large-sized stationary energy storage, an object for munitions, and an object for the universes besides these noncommercial uses.

[0011]

[Embodiment of the Invention]An example is given to below and this invention is explained.

[0012](Example 1) As a conducting agent of an anode, the material which composite-ized black lead, the following six kinds of compounds, aluminum,  $\text{CrO}_2$ ,  $\text{TiN}$ ,  $\text{B}_4\text{C}$ ,  $\text{MoB}$ , and  $\text{TiSi}_2$  was used. Weighing of black lead and the composite-ized compound was carried out to the weight ratio 1:4, and by the planetary ball mill, under the number of rotations of 250 rpm, and argon atmosphere, 15 time processings were carried out and it composite-ized. The polyvinylidene fluoride (7 % of the weight) of this compound conducting agent (6 % of the weight), positive-active-material  $\text{LiCoO}_2$  (87 % of the weight), and a binder was kneaded for 30 minutes with the stone milling machine, and it was considered as positive electrode mixture. This mixture was applied to both sides of 20-micrometer-thick aluminium foil, and it was considered as the anode. What carried out the double spread of the mixture which kneaded the polyvinylidene fluoride (7 % of the weight) of black lead (93

% of the weight) and a binder with the stone milling machine for 30 minutes to 30-micrometer copper foil in thickness was used for the negative electrode. Positive/negative two poles carried out rolling molding with the pressing machine, and after they carried out spot welding of the terminal, they were dried at 150 °C for 5 hours. The anode and the negative electrode were laminated via the separator made from microporous polypropylene, this was wound spirally, and it inserted in the battery can. The negative pole terminal was welded to the battery can, and the positive pole terminal was welded to the battery lid. What dissolved  $\text{LiPF}_6$  in the mixed solvent of ethylene carbonate and diethyl carbonate at 1 molar concentration was used for the electrolysis solution. The cylindrical shape cell was produced for the battery lid in total after pouring in an electrolysis solution in a battery can. The rate characteristic examination was presented with the cell on condition of the charge voltages 4.2V and the discharge voltage 2.7V. The rate characteristic examination was done on five conditions of 0.25C, 0.5C, 1C, 2C, and 3C. A result is shown in Table 1. Service capacity showed 0.25C as 100%.

[0013]  
[Table 1]

表 . 1

	複 合 導 電 剤	放 電 レ ー ト C ( % )				
		0 . 2 5 C	0 . 5 C	1 C	2 C	3 C
実施例 1	A l / 黒鉛	1 0 0	9 9	9 9	9 6	9 0
	C r O <sub>2</sub> / 黒鉛	1 0 0	9 8	9 8	9 5	9 0
	T i N / 黒鉛	1 0 0	9 9	9 8	9 5	8 9
	B <sub>4</sub> C / 黒鉛	1 0 0	9 9	9 8	9 4	8 9
	M o B / 黒鉛	1 0 0	9 9	9 9	9 5	8 8
	T i S i <sub>2</sub> / 黒鉛	1 0 0	9 8	9 8	9 4	8 9
比較例 1	黒鉛	1 0 0	9 5	9 0	7 8	6 8

[0014](Comparative example 1) The polyvinylidene fluoride (7 % of the weight) of black lead (6 % of the weight) of a conducting agent, positive-active-material  $\text{LiCoO}_2$  (87 % of the weight), and a binder was kneaded with the stone milling machine for 30 minutes, and it was considered as positive electrode mixture. Battery construction and cell manufacturing methods, such as a negative electrode except having used black lead for the conducting agent and an electrolysis solution, are the same as that of Example 1. The rate characteristic test result of the manufactured cell is shown in Table 1 with the result of Example 1. When the compound conducting agent of Example 1 is used, about 90% of capacity is held also with the discharge rate of 3C, but when a black lead independent conducting agent is used, it is a discharge rate of 2C and about 80% and capacitance retention have already fallen.

[0015](Example 2) As a conducting agent of an anode, the material which composite-ized black lead, the following six kinds of compounds, Ti, NbO, VN, SiC,  $\text{CrB}_2$ , and  $\text{MoSi}_2$  was used.  $\text{LiMn}_2\text{O}_4$  was used for positive active material and amorphous carbon was respectively used for negative electrode active material. In addition, battery construction material and a cell manufacturing method are the same as Example 1. The result of a rate characteristic is shown in Table 2.

[0016]  
[Table 2]

表 2

	複合導電剤	放電レートC (%)				
		0.25C	0.5C	1C	2C	3C
実施例2	Ti/黒鉛	100	98	97	94	88
	NbO/黒鉛	100	98	98	94	87
	VN/黒鉛	100	99	98	95	89
	SiC/黒鉛	100	99	98	94	89
	CrB <sub>2</sub> /黒鉛	100	98	99	96	90
	MoSi <sub>2</sub> /黒鉛	100	99	98	94	89
比較例2	黒鉛	100	94	88	77	66

[0017](Comparative example 2) The cell was produced like Example 2 except having used black lead for the anode conducting agent. The result of a rate characteristic is shown in Table 2 with Example 2. When the compound conducting agent of Example 2 is used, about 90% of capacity is held also with the discharge rate of 3C, but when a black lead independent conducting agent is used, capacitance retention is falling with a little less than 70% with the discharge rate of 3C a little less than 80% with the discharge rate of 2C.

[0018](Example 3) As a conducting agent of an anode, the material which composite-sized amorphous carbon, the following six kinds of compounds, Zr, MoO<sub>2</sub>, ZrN, TiC, ZrB<sub>2</sub>, and VSi<sub>2</sub> was used. LiNi<sub>0.9</sub>Co<sub>0.1</sub>O<sub>2</sub> was used for positive active material, and Ag support black lead was respectively used for negative electrode active material. In addition, battery construction material and a cell manufacturing method are the same as Example 1. The result of a rate characteristic is shown in Table 3.

[0019]

[Table 3]

表 3

	複合導電剤	放電レートC (%)				
		0.25C	0.5C	1C	2C	3C
実施例3	Zr/非晶質炭素	100	100	99	96	91
	MoO <sub>2</sub> /非晶質炭素	100	99	99	95	90
	ZrN/非晶質炭素	100	99	98	96	92
	TiC/非晶質炭素	100	100	98	95	90
	ZrB <sub>2</sub> /非晶質炭素	100	99	99	95	90
	VSi <sub>2</sub> /非晶質炭素	100	100	99	96	91
比較例3	非晶質炭素	100	97	93	82	71

[0020](Comparative example 3) The cell was produced like Example 3 except having used amorphous carbon for the anode conducting agent. The result of a rate characteristic is shown in Table 3 with Example 3. When the compound conducting agent of Example 3 is used, a little more than 90% of capacity is held also with the discharge rate of 3C, but when an amorphous carbon independent conducting agent is used, capacitance retention is falling with a little more than 70% with the discharge rate of 3C a little more than 80% with the discharge rate of 2C.

[0021](Example 4) As a conducting agent of an anode, the material which composite-sized amorphous carbon, the following six kinds of compounds, aluminum, WO<sub>2</sub>, ZrN, WC, TiB<sub>2</sub>, and WSi<sub>2</sub> was used. LiMn<sub>1.9</sub>Co<sub>0.1</sub>O<sub>4</sub> was used for positive active material, and Ag support amorphous carbon was respectively used for negative electrode active material. In addition, battery construction material and a cell manufacturing method are the same as Example 1. The result of a rate characteristic is shown in Table 4.



[0022](Comparative example 4) The cell was produced like Example 4 except having used amorphous carbon for the anode conducting agent. The result of a rate characteristic is shown in Table 4 with Example 4.

[0023]

[Table 4]

表 4

	複合導電剤	放電レートC (%)				
		0.25C	0.5C	1C	2C	3C
実施例 4	Al / 非晶質炭素	100	99	98	95	90
	WO <sub>3</sub> / 非晶質炭素	100	100	99	96	91
	NbN / 非晶質炭素	100	99	99	95	91
	WC / 非晶質炭素	100	99	98	95	90
	TiB <sub>2</sub> / 非晶質炭素	100	100	99	96	92
	WSi <sub>2</sub> / 非晶質炭素	100	100	99	95	90
比較例 4	非晶質炭素	100	96	91	83	70

[0024]When the compound conducting agent of Example 4 is used, a little more than 90% of capacity is held also with the discharge rate of 3C, but when an amorphous carbon independent conducting agent is used, capacitance retention is falling with 70% with the discharge rate of 3C a little more than 80% with the discharge rate of 2C.

[0025]

[Effect of the Invention]A cell with a good rate characteristic is obtained by this invention, and, thereby, the characteristic stable to consumption of the high currents at the time of starting of a portable device or departure of an electromobile, etc. is obtained.

---

[Translation done.]